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SOME REMARKS ON THE STERNHEIMER POTENTIAL*

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ABSTRACT

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The definition of the Sternheimer potential is generalized
to include wave functions which involve the spin.

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In his work on polarizabilities, shielding constants, and the like, Sternheimer¹ was led to introduce a local² potential associated with an arbitrary one-electron wave function $\psi(\vec{r})$ according to

$$(V - E_0) = - \frac{1}{\psi} (T\psi) \quad (1)$$

Here T is the (one-electron) kinetic energy operator and E_0 is defined by $V \rightarrow 0$ as $|x| \rightarrow \infty$. With this definition then ψ satisfies the Schrödinger equation.

$$H_0 \psi \equiv (T + V) \psi = E_0 \psi \quad (2)$$

In recent years Sternheimer's definition has been taken over uncritically in various formal discussions⁴ of perturbation problems involving many-electron wave functions. In particular little attention has been paid to the fact that the formula (1), with T now the total kinetic energy operator, is meaningless when applied to wave functions involving spin since the reciprocal of a spin function is undefined.

In what follows we wish then to generalize (1) to wave functions involving spin. We should also point out that exhibiting H_0 explicitly is of interest even in the rather wide class of perturbation problems (see for example reference 4, section IV) in which one can eliminate explicit mention of H_0 from the equations provided V is local since still,

one's a priori expectations as to the convergence of the perturbation theory will be determined by the relationship between the actual Hamiltonian and H_0 (see also the first reference of Footnote 5).

As the simplest case, suppose the spin part of ψ can be factored: $\psi = f \chi$, where χ is the spin function. Then the natural replacement for (1) is simply

$$(V - E_0) = -\frac{1}{f}(Tf) \quad (3)$$

Even in this simple case, however, V may have unexpected properties. In particular for N electrons it may be an N -body potential. Thus, for example, consider the Slater determinant

$$\psi = \begin{vmatrix} \varphi_1(\vec{x}_1)\alpha(1) & \varphi_1(\vec{x}_2)\alpha(2) \\ \varphi_2(\vec{x}_1)\alpha(1) & \varphi_2(\vec{x}_2)\alpha(2) \end{vmatrix} = [\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)]\alpha(1)\alpha(2)$$

Here one might expect that V is a one-body potential:

$V = v(\vec{x}_1) + v(\vec{x}_2)$ but, as one readily sees, unless φ_1 and φ_2 are both eigenfunctions of the same local one-body potential v , i.e. unless

$$\frac{1}{\varphi_1}(T\varphi_1) = \frac{1}{\varphi_2}(T\varphi_2) + \text{constant}$$

V will be a two-body potential.⁵

Now let us turn to the case in which ψ is not factorable. Let us suppose for simplicity that it is an eigenfunction of total spin, eigenvalue S , and of the Z-component of spin with eigenvalue m . Then we can write

$$\psi = \sum_{\alpha} f_{\alpha} \chi_{\alpha}^{S,m}$$

where the f_{α} involve only spatial coordinates and where the $\chi_{\alpha}^{S,m}$ are a set of orthogonal spin functions.

A natural extension of (3) is then to write

$$(V - E_0) = - \sum_{\alpha} \frac{1}{f_{\alpha}} (T f_{\alpha}) \pi_{\alpha}^{S,m} \quad (4)$$

where the $\pi_{\alpha}^{S,m}$ are spin projection operators

$$\pi_{\alpha}^{S,m} \chi_{\alpha'}^{S,m} = \chi_{\alpha}^{S,m} \delta_{\alpha\alpha'}$$

We also define them to yield zero when acting on spin functions having different total spin or Z-component. These last two requirements are, of course, not necessary for our purposes and in effect we drop them in (i) and (iii) below. However, it allows a more systematic discussion since we can then express

$\pi_{\alpha}^{S,m}$ in a general way as

$$\pi_{\alpha}^{S,m} = \chi_{\alpha}^{S,m} \chi_{\alpha}^{S,m \dagger}$$

$\pi_{\alpha}^{S,m}$ can also, in any particular case, be written in terms of electron spin operators.

With these definitions then it follows that (2) is satisfied. However, the relatively simple definition (4) has certain difficulties:

(i) It does not commute with the total spin vector because the Z-direction has been singled out. This can be remedied by replacing it by

$$(V - E_0) = - \sum_{\alpha} \frac{1}{f_{\alpha}} (T f_{\alpha}) \sum_m \pi_{\alpha}^{S,m}$$

With this definition we clearly still have (2) and in addition, if the $\pi_{\alpha}^{S,m'}$ for $m' \neq m$ are derived from $\pi_{\alpha}^{S,m}$ by the appropriate spin raising and lowering operators, one readily verifies that $(V - E_0)$ commutes with the total spin vector.

(ii) In general it is not symmetric in the particles. This we remedy as follows: Since Ψ is antisymmetric and T symmetric it follows from (2) that

$$[T + P(V - E_0)] \Psi = 0$$

where $P(V - E_0)$ is derived from $(V - E_0)$ by some permutation of particle labels. Summing over P and dividing by $N!$ we get again an equation of the form (2) where now $(V - E_0)$ is the symmetric operator

$$V-E_0 = -\frac{1}{N!} \sum_p P \left[\sum_{\alpha} \frac{1}{f_{\alpha}} (T f_{\alpha}) \sum_m \pi_{\alpha}^{S,m} \right] \quad (5)$$

(iii) The one remaining obviously peculiar feature of this definition of $V-E_0$ is that it yields zero identically when applied to any wave function having total spin other than S , expressing the fact that the extension to other spin is quite arbitrary, and so we do not discuss it further.⁶

This is pretty much our final result save for two comments below. We would stress its complicated structure even if ψ is a single determinant (recall footnote 5.) In general, although local it may well be an N-body, spin dependent-potential. We close with three comments:

(iv) Suppose we had written

$$\psi = \sum_{\alpha'} f_{\alpha'} \chi_{\alpha'}^{S,m}$$

where the $\chi_{\alpha'}^{S,m}$ are related to the $\chi_{\alpha}^{S,m}$ by a real (see (V) below) orthogonal transformation. It can be shown by a simple example that following the same procedure but using the primed quantities, will lead to a different $V-E_0$.

(v) So far we have not discussed the Hermitian properties of $V-E_0$. If the f_{α} are real, $(V-E_0)$ as defined is Hermitian. If we cannot choose the f_{α} to be real this will usually imply that the f_{α} involve not only "internal

coordinates" but also have reference to some fixed directions in space, i.e. they involve "external coordinates" (for example Euler angles in the case of an atom) and are not invariant under the relevant symmetry group (Rotations for an atom). For such cases we can usually write

$$f_{\alpha} = \sum_A g_{\alpha A} Y_A^{L, \mu}$$

where the $g_{\alpha A}$ are real functions of internal coordinates and the $Y_A^{L, \mu}$ are functions of the external coordinates, the L and A designating a particular irreducible representation of the symmetry group, and μ denoting a particular member of the irreducible basis (A, L, μ are exactly analogous to α, S, m). Further one will usually have that

$$\frac{1}{g_{\alpha A} Y_A^{L, \mu}} T(g_{\alpha A} Y_A^{L, \mu}) = \frac{1}{g_{\alpha A}} (T_{A, L}^{INT} g_{\alpha A}) \quad (7)$$

where $T_{A, L}^{INT}$ is an internal kinetic energy operator which may depend on A and L but not on μ . After these remarks it is clear that a Hermitian generalization of (5) is to replace

$$\frac{1}{f_{\alpha}} (T f_{\alpha}) \text{ by}$$

$$\sum_A \frac{1}{g_{\alpha A}} (T_{A, L}^{INT} g_{\alpha A}) \sum_{\mu} \pi_A^{L, \mu}$$

where we have introduced the sum on μ in order to make our

potential invariant under the symmetry group.

Remarks analogous to (iii) and (iv) are applicable to this definition.

(vi) This last potential is almost certainly not strictly local. The net result of the external coordinate projection operators will usually be to bring in angular momentum operators and probably also integral operators. So for this case we have not succeeded in attaining the original objective.

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FOOTNOTES

1. R. Sternheimer, Phys. Rev. 96, 951 (1957). See also R. Makinson and J. Turner, Proc. Phys. Soc. (London) A66, 857 (1953).
2. A local potential is strictly speaking, one which involves neither momentum operators nor integral operators though usually only the latter restriction is implied.
3. In what follows we will not consider the definition of V and E_0 separately. For the purposes of Schrödinger perturbation theory only the combination of $T + V - E_0 = H_0 - E_0$ is needed.
4. See for example. J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Recent Advances in Quantum Chemistry, vol. I (Academic Press, New York, 1964).
5. On the other hand if we are dealing with a single Slater determinant we can always find a one-body non-local potential such that (2) is satisfied. See S. T. Epstein, J. Chem. Phys., 41, 1045 (1964), and G. C. Ghirardi and A. Rimini, J. Math. Phys. 5, 722 (1964).
6. In the (unlikely) case that the f_α are all degenerate eigenfunctions, eigenvalue ϵ , of the same symmetric potential then our definition yields

$$(V - E_0) = (W - \epsilon) \sum_{\alpha} \sum_m \pi_{\alpha}^{S, m}$$

Then the natural extension, of course, is to replace the double sum, which is the projection operator for wave functions of spin S , by the unit operator, and hence identify V with W and E_0 with ϵ .